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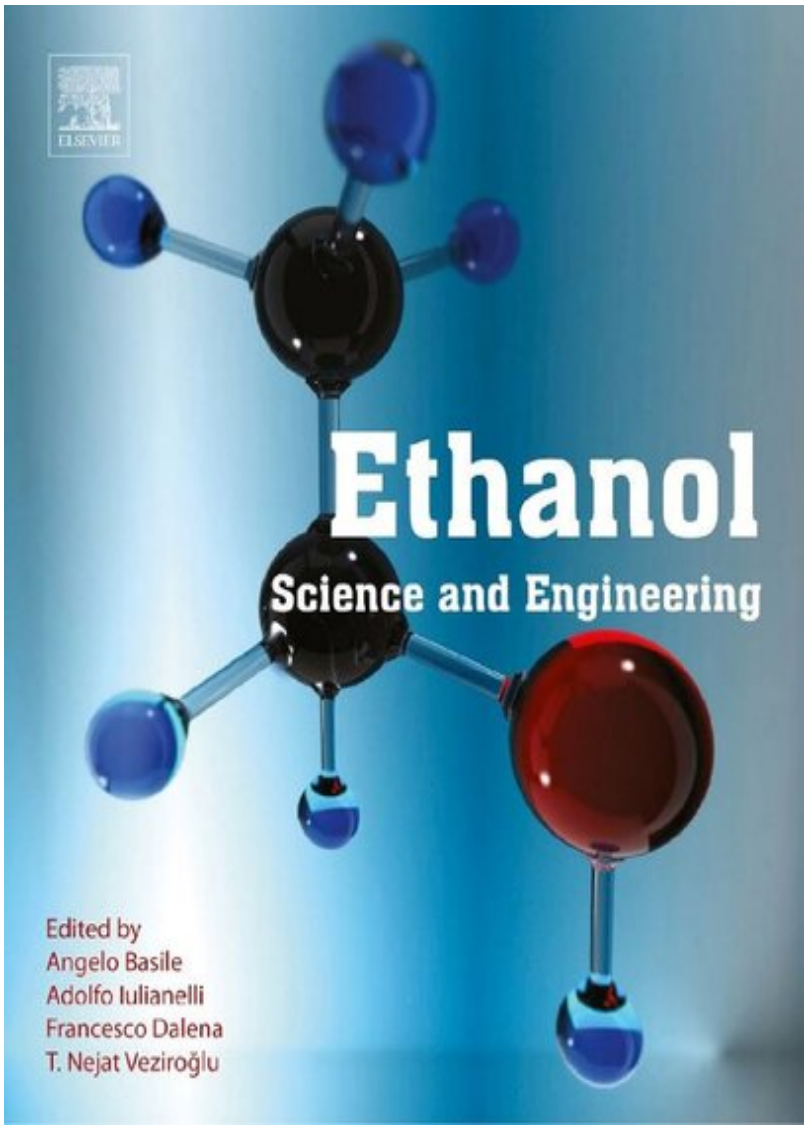


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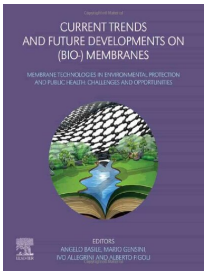


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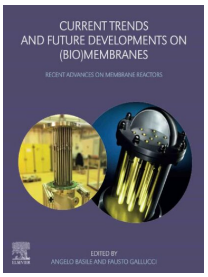


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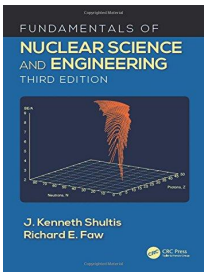


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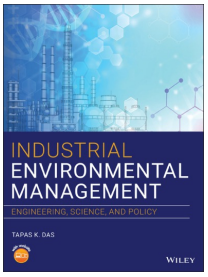


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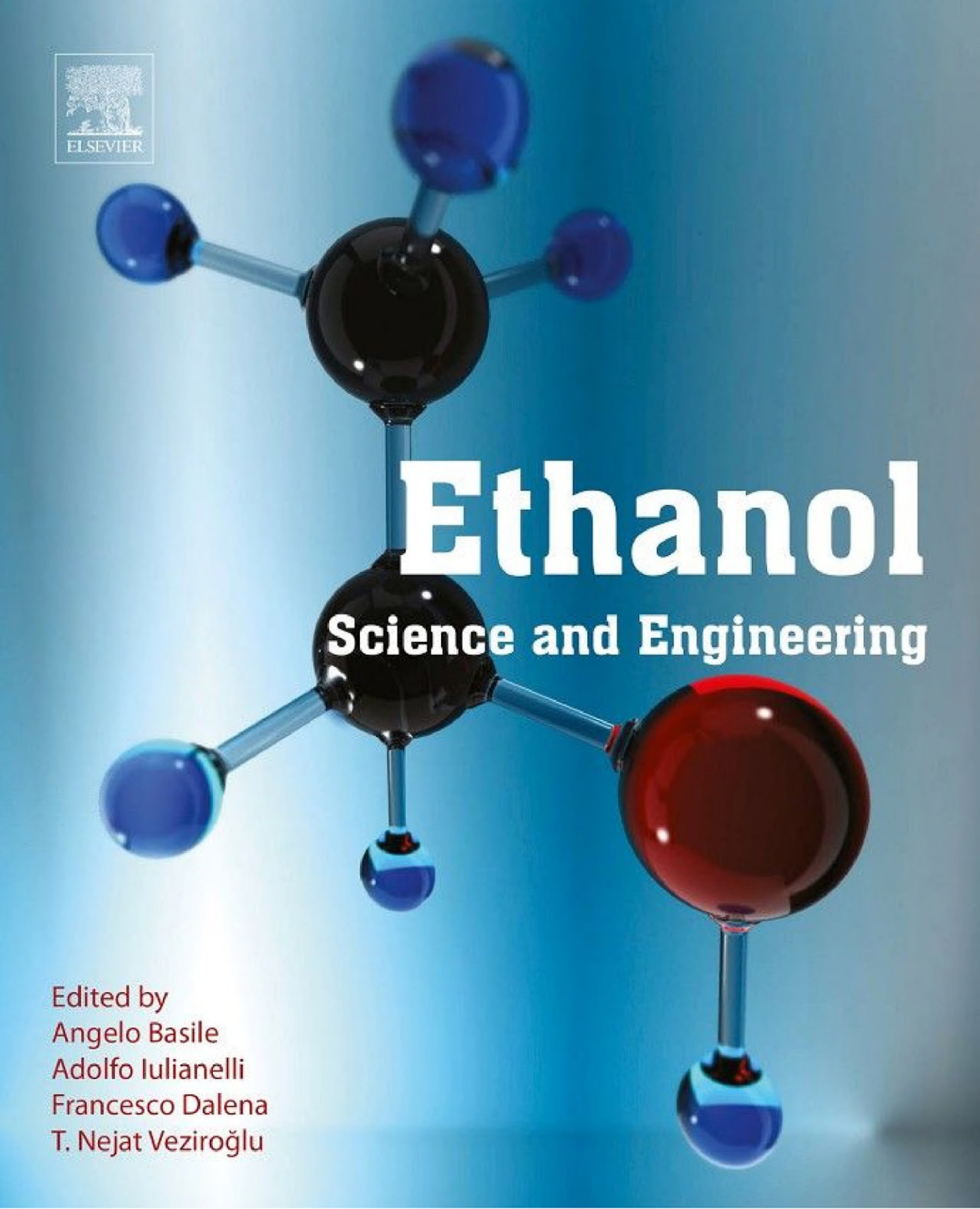
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# Ethanol
## Science and Engineering

*Edited by*

**Angelo Basile**

**Adolfo Iulianelli**

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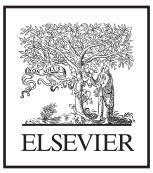

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The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
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**Library of Congress Cataloging-in-Publication Data**
A catalog record for this book is available from the Library of Congress

**British Library Cataloguing-in-Publication Data**
A catalogue record for this book is available from the British Library

ISBN: 978-0-12-811458-2

For information on all Elsevier publications visit our website at https://www.elsevier.com/books-and-journals

*Publisher:* Susan Dennis
*Acquisition Editor:* Kostas Marinakis
*Editorial Project Manager:* Carly Demetre
*Production Project Manager:* Nilesh Kumar Shah
*Cover Designer:* Vicky Pearson Esser

Typeset by TNQ Technologies

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# Preface

The rapid growth in global energy demand, greenhouse gas emissions, and global warming, associated with the use of fossil fuels, is stimulating a continuous research for alternative and renewable fuels showing a very low environmental impact.

In addition, nowadays, the energy dependence on fossil fuels creates a strong instability in the global market because the world reserves of fossil fuels are running out with a relative instability of fuel prices.

At present, ethanol is considered a viable competitor over those derived from fossil fuels, representing one of the best biofuels for transportation. Indeed, it can be burned directly or blended with petrol to improve fuel combustion in vehicles, resulting in lower $CO_2$ emission to reduce greenhouse gases in the atmosphere. Furthermore, ethanol is not only considered an excellent fuel but also it represents an extreme versatile chemical product. It is an important raw material for both food processing and the production of chemical products, and it is also particularly used in the pharmaceutical industry. Its applications increase day by day and turn out to be of crucial importance from a world research point of view. The aim of this book is to provide, with contributions coming from some of the most representative scientists in the field, an overview on the state of the art about the most recent researches on ethanol production, application, and its economical role in the global market as deeply discussed in the dedicated four sections of this book.

In the first section (*Science and Production*), Chapter 1 (Abdulrazzaq and Schwartz) describes the catalytic conversion of ethanol to commodity and specialty chemicals of industrial and commercial interest. Chapter 2 (Dalena, Senatore, Iulianelli, Di Paola, M. Basile, and A. Basile) gives an overview on the ethanol production processes and their future perspectives related to the biomass exploitation. Chapter 3 (A. Küüt, Ritslaid, K. Küüt, Ilves, and Olt) deals with an overview about the state of the art on the conventional processes for ethanol production. Chapter 4 (Jalilnejad and Ghasemzadeh) concludes the first section of the book with bioethanol production process and the criticisms related to the food versus fuel utilization.

In the second section (*Application and Innovation*), Chapter 5 (Liu, Senanayake, and Rodriguez) involves a review on the most common catalysts used in the ethanol reforming processes. Steam reforming, partial oxidation, and autothermal reforming of ethanol for hydrogen production in conventional reactors are the topics dealt with in Chapter 6 (Vita, Pino, Italiano, and Palella), in which the most important ethanol reforming processes in the field of hydrogen production are reviewed. The same topic was discussed using membrane reactors technology in Chapter 7 (Iulianelli, Dalena, and Basile), giving details about the benefits of this technology over the conventional systems. In Chapter 8 (Ilves, Küüt, and Lot), ethanol utilization as an internal combustion engine fuel is extensively discussed, while Chapter 9 (Borole) deals with the opportunities given by the ethanol exploitation for electricity and hydrogen production via bioelectrochemical systems. Chapter 10 (Lazar, Senila, Dana, and Mihet) describes the challenges of using crude bioethanol for hydrogen

production by ethanol steam reforming reaction, pointing out the benefits and drawbacks of this approach. Section two concludes with Chapter 11 (Meng), which is dedicated to ethanol utilization in automotive applications, including the environmental impacts of ethanol exploitation in terms of air pollution and greenhouse gas emissions as well.

Section three of the book (*Modelling and Technology*) starts with Chapter 12 (Ghasemzadeh, Jalilnejad, and Tilebon), in which the opportunities given by ethanol exploitation in the field of hydrogen production technologies are reviewed. Chapter 13 (Vaidya, Wu, and Rodrigues) analyzes from a kinetic point of view ethanol production processes for hydrogen production. Chapter 14 (Gallucci, Pacheco Tanaka, and van Sint Annaland) illustrates ethanol reforming in thermally coupled, fluidized bed, bubble column, and membrane reactors, reviewing the advantages and disadvantages of each kind of reactor to produce high-grade hydrogen.

The topic of Chapter 15 (Cermenek, Ranninger, and Hacker) is represented by the alkaline direct ethanol fuel cell, which represents a promising environment-friendly energy converter for the production of clean and efficient power. Chapter 16 (Contestabile) contributes to this book pointing out the role of bioethanol utilization in batteries, hydrogen fuel cells, and passenger cars, whereas Chapter 17 (Rahimpour, Keshtkari, and Aryafard) points out the benefits and unsolved issues regarding ethanol as a potential substitute to current aviation fuel.

The last section of this book (*Environment and Economy*) starts with Chapter 18 (Amiri and Ghasemzadeh), in which the authors describe the impact of an ethanol economy on the environment as well as on demand and marketing. Chapter 19 (Kohler) undertakes an economic assessment of ethanol production based on the volatile nature of international crude oil prices, growing global concerns over energy security, and GHG emissions. Last but not less important, Chapter 20 (Mihăilă-Ştefănescu) ends this book presenting a technical and economic comparison of bioethanol exploitation within agriculture and industry.

In conclusion, the editors appreciate the hard work done by the authors and wish to thank them all for the fruitful cooperation in the preparation of this book. The authors also thank all the staff of Elsevier for their precious and irreplaceable help in preparing, step by step, this volume.

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CHAPTER

# 1 Catalytic Conversion of Ethanol to Commodity and Specialty Chemicals

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## CHAPTER OUTLINE

**1. Introduction** ..... 3
**2. Products From Direct Ethanol Conversion: Commodity Chemicals** ..... 5
2.1 Ethylene ..... 5
2.2 Propylene ..... 6
2.3 Acetaldehyde ..... 7
2.4 Acetic Acid and Ethyl Acetate ..... 8
**3. Products From Ethanol Dimerization and Oligomerization: High-Value Commodities and Specialty Chemicals** ..... 10
3.1 Butadiene ..... 10
3.2 Butanol, Higher Alcohols, and Aromatics ..... 13
3.3 Lubricants ..... 17
**4. Conclusion and Future Trends** ..... 18
**List of Abbreviation** ..... 19
**References** ..... 19

## 1. INTRODUCTION

Using renewable resources for producing fuels and high-value chemicals is an important next step for the chemical industry because of the finite nature of global natural gas and petroleum resources. In addition, the use of fossil resources as the primary source for fuels and chemicals has led to long-term environmental concerns. In particular, the use of petroleum-derived fuels is widely recognized as the main driver for increased levels of carbon dioxide in the atmosphere. Several alternatives to fossil-based resources have been proposed for the production of fuels and chemicals, among which biomass is the most prominent (Chheda et al., 2007; Huber et al., 2006; Alonso et al., 2010; Luterbacher et al., 2014). However, recent developments in enhanced oil and gas recovery have mitigated concerns about the availability of carbon for fuel production (Gerard, 2016; Wood et al., 2012), although the impact on the chemical industry has been

**Ethanol.** https://doi.org/10.1016/B978-0-12-811458-2.00001-8
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somewhat more complex. Although the availability of cheap natural gas liquids has led to interest in building new ethane crackers in the United States (Greenwood, 2016), there has been a concomitant shift in the availability of industrial chemicals with four or more carbons (Siirola, 2014). Thus, there remains a desire to use biomass as a feedstock for chemical production. In particular, strategies that combine both chemical and biological catalysis offer significant flexibility to selectively retain the functionality native in biomass and efficiently produce high-value chemicals from biomass (Schwartz et al., 2014, 2016; Shanks and Keeling, 2017). A general feature of such strategies is the use of biologically derived platform molecules that can be upgraded to several different end products.

The choice of the target product is a nontrivial consideration when converting biomass to chemicals. There have been many reports of the conversion of biomass into industrial commodity chemicals such as olefins, hydrogen, methane, etc. (Rass-Hansen et al., 2007; Christensen et al., 2008). However, it would be difficult to completely meet the demand for ethylene, for example, if biomass is used as the sole feedstock. As a conveniently available reference metric, one can compare the 350 million metric tons corn grown in the United States in 2013 (Capehart, 2017) with the 143 million metric tons ethylene produced worldwide that same year (True, 2013). Recognizing that the mass yield of ethanol from glucose is approximately 50 wt%, replacing fossil-based ethylene with biobased ethylene would require redirecting nearly all of the corn produced in the United States (as a representative biomass feedstock and assuming it is 100% starch). Consequently, it is more appropriate to choose lower volume, higher value chemical products to target for research.

Ethanol is suitable for use as a platform chemical because it can be converted to many different end products. Bioethanol can be obtained from biomass resources by fermentation of raw materials such as corn, sugarcane, and lignocellulose. The push to produce fuel ethanol from biomass has led to the development of microorganisms that can convert diverse biomass feedstocks to ethanol (Geddes et al., 2011). In this chapter, we will highlight important catalytic processes for the conversion of this bioethanol to both commodity and specialty chemicals. The aim is not to provide an exhaustive review but, rather, to focus on processes that are historically significant and emerging technologies that have the potential to fill the gaps left by changes in petroleum feedstocks that have occurred in the first two decades of the 21st century. Historically, ethanol has been upgraded directly to $C_2$−$C_4$ species using relatively simple reactions (i.e., via dehydration, dehydrogenation, etc.). Recent trends have expanded on this chemistry to obtain high−carbon number species. Our discussion will begin with the direct conversion pathways that generally produce commodity chemicals and conclude by highlighting recent advances in oligomerization chemistry that lead to higher value specialty chemicals and lubricants.

# 2. PRODUCTS FROM DIRECT ETHANOL CONVERSION: COMMODITY CHEMICALS

## 2.1 ETHYLENE

Ethylene is one of the most significant commodity chemical in production today. It is the platform molecule of choice for the synthesis of polyethylene, polyvinyl chloride, polyethylene terephthalate, polystyrene, ethylene glycol, ethylbenzene, and many other chemical products. Ordinarily, ethylene is produced industrially by cracking naphtha and gas oils, with approximately 98%–99% of world production based on this method. Currently, the shale gas revolution has shifted attention to the use of ethane as a feedstock, which is abundant in many shale wells. The importance of steam cracking of ethane has increased dramatically in recent years, and it is considered to be a productive alternative route for ethylene production. Leading up to this shift, many technologies and methods were developed to use alternative resources for ethylene production instead of using conventional cracking processes (Drumm, 2006; Sanders et al., 2007), and some technology development in this area continues to this day.

In the years following the Second World War, the practice of ethylene production via ethanol dehydration was not uncommon, and in the intervening years the dehydration reaction has been evaluated using many different types of catalysts such as metal oxides, alumina, clays, silica, H-ZSM-5 and other zeolites, amorphous silica alumina, and phosphates, among others (Rass-Hansen et al., 2007; Zhang and Yu, 2013; Angelici et al., 2013; Morschbacker, 2009).

Ethanol dehydration is an endothermic reaction requiring high temperatures, generally reported in the range of 473–723 K (Angelici et al., 2013). The most challenging factor in ethanol dehydration is the tendency to produce side products such as diethyl ether. In particular, high-temperature reactions lead to ethylene whereas low-temperature reactions tend to increase the possibility of forming diethyl ether and other products.

A variety of catalysts have been tested for this process. Early reports focused on phosphoric acid (Morschbacker, 2009), whereas more recent studies have shown that alumina-containing catalysts are the most promising. In particular, H-ZSM-5 afforded a high yield of about 95% (Bi et al., 2010; Zhang et al., 2008) compared with $\gamma$-$Al_2O_3$, which gave a yield of approximately 80% at low temperatures (Angelici et al., 2013). Other catalytic systems have also been examined for low-temperature dehydration. Silicoaluminophosphate (SAPO) catalysts doped with $Mn^{2+}$ and $Zn^{2+}$ showed 97.8% yield of ethylene at 613 K (Chen et al., 2010). Zhang et al. (2008) probed four different catalysts, $Al_2O_3$, H-ZSM-5, Silicoaluminophosphate-34 (SAPO-34), and Ni-doped SAPO-34 (NiSAPO-34), and tested them under different conditions. The most active catalysts were H-ZSM-5

and NiSAPO-34. Both showed high selectivity and greater than 90% yield toward ethylene, whereas the others showed low selectivity. The authors attributed the low selectivity over the other catalysts to an abundance of strong acid sites in their structures. Alumina is one of the most active catalysts for this reaction, with ethylene production occurring in a temperature range of 300−500°C, obtaining high ethylene yields between 94% and 99% (Zhang and Yu, 2013).

## 2.2 PROPYLENE

In addition to ethylene, it is also possible to also produce higher olefins from ethanol. The success of the ExxonMobil (formerly Mobil) Methanol-to-Olefins process has driven the use of H-ZSM-5 as a catalyst for the conversion of ethanol to propylene. In particular, the group of Tadahiro Fujitani has been quite prolific in this area. As early as 2009, their group showed that H-ZSM-5 is active for the production of propylene from ethanol using commercial zeolites purchased from Zeolyst (Song et al., 2009). The highest selectivities observed in that work were ∼30% and obtained using a Zr-impregnated H-ZSM-5, which the authors attribute to the presence of moderately acidic active sites that promote the formation of $C_{3+}$ hydrocarbons from ethanol. In a follow-up study, this group synthesized a series of zeolites with Mordenite Framework Inverted (MFI) topology, and they concluded that the reactivity is independent of the acid site density (i.e., all acid sites in these catalysts are equally active for this reaction) (Xia et al., 2010). The use of metal-containing H-ZSM-5 zeolites also leads to ∼30% selectivity in the reaction. For example, the propylene yield using Sr−HZSM-5 was 32% at complete ethanol conversion. This material showed similar stability to the Zr-impregnated zeolite (Goto et al., 2010).

Similar results were obtained by Inoue et al. (2010) using low−Al content H-ZSM-5 catalysts. Impregnation of these catalysts with La led to similar selectivities of ∼30%. Importantly, deactivation was observed for all the catalysts described thus far, although the La-promoted catalyst of Inoue's group is qualitatively more stable than the Zr-promoted material from Fujitani et al.

Motivated by the previous success of phosphorous impregnation of ZSM-5 to improve stability in other reactions, Fujitani et al. evaluated this same catalyst for propylene formation (Song et al., 2010). Similar propylene selectivities were obtained (∼30% maximum), although catalyst deactivation was eliminated during short (∼8 h) reactions. In a follow-up study (Takahashi et al., 2012), this same group showed that the P-containing H-ZSM-5 catalyst deactivates only slightly over the course of 100 h of time-on-stream, whereas an unpromoted H-ZSM-5 catalyst loses all of its activity within 20 h at the same conditions. They note that the improved stability is dependent on the presence of water vapor in the reactor.

Direct conversion of ethanol to propylene is not the only process available. Before the development of the ZSM-5−based catalysts described earlier, Braskem undertook development of a biomass-derived ethanol-to-propylene process. In their route, ethanol is first dehydrated to ethylene, which is oligomerized to butene.

Using the Lummus process, the butene is subsequently converted to propylene and ethylene via olefin metathesis (Bruijnincx and Weckhuysen, 2013). It is worth noting, though, that the prevalence of cheap shale gas in the United States in the early part of the 21st century has made both bioethanol-to-ethylene and bioethanol-to-propylene processes economically unattractive. Notably, a significant amount of propane is recovered with methane and ethane in shale gas, and there is well-established technology (i.e., Houdry dehydrogenation for converting propane to propylene and steam cracking for converting ethane to ethylene) that may be more economically attractive as long as shale gas liquids are inexpensive relative to lignocellulose.

## 2.3 ACETALDEHYDE

Acetaldehyde is another significant chemical that can be produced catalytically from ethanol. It is a commodity chemical which is commonly used as an intermediate in the synthesis of important industrial chemicals, such as acetic acid, ethyl acetate, crotonaldehyde, butadiene, pentaerythritol, butylene glycol, and many others (Sun and Wang, 2014). Importantly, because ethanol is natively oxygenated, production of acetaldehyde from ethanol avoids the hazards associated with hydrocarbon oxidation.

Historically, acetaldehyde has been produced commercially by hydrating acetylene to vinyl alcohol, which then tautomerizes to acetaldehyde (Wittcoff, 1983). This process was often performed in the presence of sulfuric acid as a catalyst. As the price of ethylene dropped in the 1960s, ethylene saw use as a raw material in the process of acetaldehyde production. In this case, acetaldehyde is produced either by hydration of ethylene to ethanol followed by dehydrogenation or by partial oxidation of ethanol with air over a silver gauze catalyst to give acetaldehyde. Currently, the most common process for acetaldehyde synthesis is the Wacker process, which directly oxidizes ethylene to acetaldehyde over palladium or copper chlorides.

Acetaldehyde can be produced biorenewably by the dehydrogenation of ethanol. This process has been performed over many different types of catalysts and has been tested at a wide range of temperatures, from 150 to 350°C. Generally, the process is highly selective using noble metals such as silver or gold. Copper has also been observed to be effective for the dehydrogenation reaction.

Guan and Hensen (2009) investigated the use of a range of silica-supported gold nanoparticle catalysts for the catalytic oxidation of ethanol. They studied the influence of both the support structure and the gold nanoparticle size in both the presence and absence of oxygen. Acetaldehyde selectivity in the absence of oxygen at temperatures below 350°C was between 60% and 80%, depending on Au particle size, at complete conversion. At 400°C the selectivity to acetaldehyde was above 90% at complete ethanol conversion regardless of the Au particle size. The best results were obtained using catalysts with midsized particles, suggesting there is an optimum in Au nanoparticle size for acetaldehyde production.

Additionally, co-feeding oxygen with ethanol led to increased activity and selectivity toward acetaldehyde relative to reactions carried out under anaerobic reactions. The highest conversion was obtained in the presence of oxygen using an MCM-41−supported Au catalyst at 250°C, which resulted in 90% selectivity toward acetaldehyde at 20% ethanol conversion. In contrast, Wittcoff previously reported the oxidation of ethanol over silver oxide or silver gauze at much higher temperatures (e.g., 480°C), with conversions ranging between 74% and 82% and selectivities to acetaldehyde of around 80% (Wittcoff, 1983).

Using $Au/TiO_2$ as catalyst leads to about 65% acetaldehyde selectivity at 35% ethanol conversion at 90°C and 42% selectivity at 95% ethanol conversion at 280°C in the presence of oxygen (Simakova et al., 2010). However, at elevated temperatures the catalyst deactivated and the selectivity to acetaldehyde was only approximately 40%. Liu and Hensen (2013) have reported that a ternary spinel $MgCuCr_2O_4$-supported gold nanoparticle catalyst is highly active and able to achieve 90% stable conversion with 85% selectivity toward acetaldehyde at 200°C.

Chang et al. (2006) have tested various loadings of copper supported on Rice Husk Ash (RHA), which has a high content of amorphous silica. At 275°C using a 5.75 wt% Cu/RHA catalyst, this group obtained over 80% ethanol conversion and nearly quantitative selectivity to acetaldehyde. The Cu/RHA was also more active than copper supported on silica gel prepared by the same procedure (Angelici et al., 2013). The improvement using RHA as a support was ascribed to changes in the particle size and surface area of the copper particles in the catalyst. Also using non−precious metal catalysts, Kim et al. (2008) studied the conversion of ethanol to acetaldehyde using vanadium−tungsten mixed oxide catalysts with various ratios of vanadium-to-tungsten. A catalyst containing 95% vanadium showed the best performance over a different range of temperatures, with the highest yield of acetaldehyde of about 90% at 300°C.

## 2.4 ACETIC ACID AND ETHYL ACETATE

Related to acetaldehyde production, ethanol can be further oxidized to acetic acid and ethyl acetate. Industrially, acetic acid is produced by either the oxidation of acetaldehyde with dioxygen or by carbonylation of methanol or methyl acetate and some is also produced by direct oxidation of butane (Wagner, 2014). Renewable acetic acid can be obtained by oxidation of ethanol-derived acetaldehyde.

Aerobic conversion of ethanol leads to mixtures of acetaldehyde, acetic acid, and ethyl acetate. Pd-based catalysts are particularly useful in this regard. For example, Gaspar et al. (2010) showed that palladium oxide supported on monoclinic zirconia (PdO/*m*-$ZrO_2$) can be used to produce acetic acid, ethyl acetate, and acetaldehyde (32%, 35%, and 25% selectivities, respectively, at 32% ethanol conversion) from ethanol at 175°C in the presence of dioxygen. Notably, the phase of the $ZrO_2$ support is significant for achieving high selectivity. Physical mixtures of the Pd-containing catalyst with other zirconias lead to a near-complete deactivation of the acetic acid

production pathway and increased production of acetaldehyde and ethyl acetate. Similarly, these authors note that the use of CuO/ZnO supported on $ZrO_2$ leads to production of acetaldehyde and ethyl acetate, but not acetic acid (regardless of the zirconia crystal structure).

Au-containing catalysts are also active for the production of acetic acid under the correct conditions. Takei et al. (2011) showed that ZnO-supported Au nanoparticles are particularly selective for acetic acid, obtaining 46% yield to acetic acid and 44% yield to acetaldehyde at complete conversion at 220°C in the vapor phase. Much of their study, though, focused on acetaldehyde production, and they obtained high yields to acetaldehyde (some in excess of 90% at complete ethanol conversion) using a variety of basic supports. Tembe et al. (2009) made similar observations in the conversion of ethanol using Au/ZnO and $Au/TiO_2$ catalysts in the liquid phase. By using a slight excess of oxygen at the start of the batch reaction, they obtained nearly quantitative yield of acetic acid from ethanol using Au/ZnO at 150°C. Similarly, Christensen et al. (2006) obtained high yields (greater than 90%) to acetic acid during liquid-phase oxidation using a $Au/MgAl_2O_4$ catalyst.

The chemistry required for producing ethyl acetate is closely related to that for producing acetic acid, and many of the works described in the earlier paragraphs also detail the production of ethyl acetate. Indeed, the conversion of acetic acid to ethyl acetate requires only a Fischer esterification, suggesting that ethyl acetate production may be catalyzed by acetic acid at the relevant reaction conditions. Au-based catalysts can be used in this regard. Zheng and Stucky (2006) observed 20% selectivity to ethyl acetate at 45% ethanol conversion using a carefully synthesized $Au/SiO_2$ catalyst, with the remainder of the selectivity going to acetaldehyde. Better selectivity can be obtained when an adequate oxidation catalyst is paired with a support containing acidic or basic sites active for Fisher esterification. The use, for example, of a Pd catalyst supported on acidic Y-zeolite leads to oxidation of ethanol to acetic acid followed by acid-catalyzed esterification (Yan and Chang, 2000). These authors obtained 49.6% selectivity to ethyl acetate at 83.3% ethanol conversion.

It is possible to obtain ethyl acetate from ethanol without passing through acetic acid as an intermediate. Interestingly, Freitas et al. (2016) obtained selectivities near 80% to ethyl acetate using $Cu{-}Ag/ZrO_2$ catalysts in the absence of added oxygen. They note that the selectivity to ethyl acetate decreases with increasing Ag loading, attributed to a silver-induced change in the copper oxidation state. Similar results were obtained by Sato et al. (2013) using monometallic $Cu/ZrO_2$ catalysts, and these authors note that the zirconia phase plays an important role in obtaining high selectivity to ethyl acetate, obtaining 80.5% selectivity at 48.9% ethanol conversion. A Cu−Zn−Zr−Al−O catalyst was reported by Inui et al. (2004) to be similarly active for acetaldehyde production. Other catalysts are also active for producing ethyl acetate along with acetaldehyde and acetic acid, and Gallo et al. (2014) provide an excellent review of which materials are active for which reaction.

## 3. PRODUCTS FROM ETHANOL DIMERIZATION AND OLIGOMERIZATION: HIGH-VALUE COMMODITIES AND SPECIALTY CHEMICALS

### 3.1 BUTADIENE

One of the more promising chemicals that can be produced from ethanol is butadiene. Butadiene is an important building block for the production of polymers such as Styrene–Butadiene Rubber, polybutadiene, and styrene butadiene latex. Approximately 95% of butadiene is currently obtained as a by-product of the naphtha cracking process used to produce ethylene. However, there are downsides to this route as a result of the complex, expensive separation process that requires several extractive distillation steps. Moreover, as discussed earlier, in the first two decades of the 21st century, there has been a shift toward lighter feedstocks for ethylene production in the United States, which has led to a decreased output of butadiene and put pressure on that market. Consequently, attention has shifted toward the use of alternative renewable resources for "on-purpose" butadiene synthesis.

The one-step process for butadiene production from ethanol was first developed in Russia in the early 20th century by Lebedev (1933). The Lebedev process for the direct conversion of ethanol into butadiene involves first dehydrogenating ethanol to acetaldehyde, followed by aldol condensation of acetaldehyde to give 3-hydroxybutanal that is subsequently dehydrated to give crotonaldehyde. Crotonaldehyde is reduced to give crotyl alcohol, which is finally dehydrated to produce butadiene, as shown in Fig. 1.1. The whole process occurs over a single catalyst in a single reactor. The Ostromislensky process was developed at Union Carbide in parallel to the Lebedev process and is referred to as the "two-step process" (Waclaw, 1944; Corson et al., 1950) wherein ethanol is dehydrogenated to acetaldehyde in one reactor followed by condensation of this acetaldehyde with the remaining ethanol to produce butadiene in a second reactor (see Fig. 1.2).

Many research groups in both the United States and Russia have tested different types of catalysts based on these commonly accepted pathways for producing butadiene. Ultimately, the one-step process proved to be less expensive and more

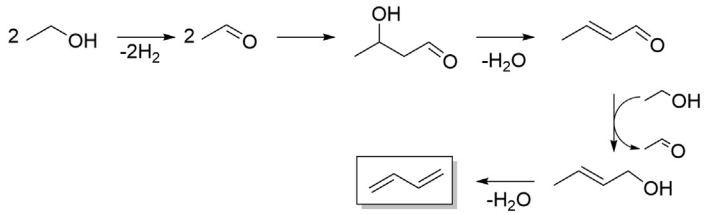


**FIGURE 1.1**

Generally accepted reaction network for the Lebedev process.

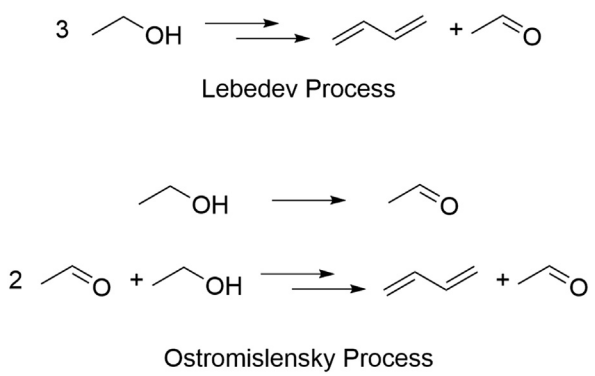


**FIGURE 1.2**

Comparison of the Lebedev process with the Ostromislensky process.

acceptable in terms of intermediate steps for producing butadiene. The Lebedev process involves a complicated network of reactions, although the network shown in Fig. 1.1 remains to be definitively proved. Recently, new attention has been paid to the Lebedev process with the aim of demonstrating the conditions and catalytically active sites that are required. It is generally accepted that the reaction requires a subtle balance of various active sites (acid, basic, and redox) together to achieve effective catalysis.

The early catalysts used for this reaction were Al−Zn mixed oxides. Quattlebaum et al. (1947) first proposed the reaction network shown in Fig. 1.1. They showed that butadiene production was more facile when using a feed mixture of ethanol and crotonaldehyde than when using a feed of acetaldehyde. Following up on this work, Bhattacharyya et al. carried out the reaction in fluidized bed reactor over an $Al_2O_3$−ZnO catalyst ($Al_2O_3$:ZnO = 60:40) and co-fed various expected intermediate components with ethanol, including acetaldehyde, crotonaldehyde, and dihydrogen (Bhattacharyya, 1967). Reactions with a pure ethanol feed were consistent with the mechanism of Lebedev, whereas those having ethanol with acetaldehyde in various ratios also led to the same butadiene productivity. Feeding crotonaldehyde with either hydrogen or ethanol both led to butadiene production as well. Thus, Bhattacharyya et al. concluded that the aldol condensation of acetaldehyde is not the rate-controlling reaction in the Lebedev pathway.

$MgO-SiO_2$ mixed oxides have also been shown to be active for butadiene production. Kvisle et al. (1988) tested a $MgO-SiO_2$ catalyst produced by wet kneading, and they obtained 30% selectivity to butadiene and 55% selectivity to ethylene at 55% ethanol conversion at steady state. This group hypothesized that adding oxygen or acetaldehyde to the ethanol feed would increase the activity toward butadiene. They proposed a mechanism parallel to that proposed by Quattlebaum et al. (1947), but their proposed rate-controlling reaction occurs before the hydrogen transfer step, which would lead to the accumulation on the surface of a $C_2$ species

and not $C_4$-oxygenated intermediates. Importantly, these authors indicate that catalyst morphology is essential for controlling the selectivity to butadiene, implying that careful catalyst preparation is critical for producing butadiene. Makshina et al. (2012) also conclude that catalyst preparation and morphology are critical for butadiene production when studying a similar $MgO-SiO_2$ system.

Recent work by Weckhuysen and Bruijnincx has focused more detail on the $MgO-SiO_2$ system, using Cu as a promoter. They concur with the observations of Kvisle et al. (1988) that the method used to prepare the mixed oxide is critical for obtaining butadiene, and they observe that promotion using CuO improves butadiene yields significantly (Angelici et al., 2014). They explain that the influence of morphology on butadiene yield is caused by variations in the number and strength of acidic and basic sites, with a small number of strongly basic sites combined with moderately acidic and basic sites leading to the highest butadiene yield (Angelici et al., 2015b). Using a series of in situ and *operando* experiments, they elucidate that the CuO added to the catalyst to improve performance forms a solid solution in the oxide support and is reduced to metallic copper during the reaction (Angelici et al., 2015a). This observation, combined with the improved performance of the Cu-containing materials, suggests that ethanol dehydrogenation may play a more important role in butadiene formation than suggested by previous work.

Sushkevich et al. (2014) have evaluated MgO, $ZrO_2$, $Nb_2O_5$, $TiO_2$, and $Al_2O_3$, all supported on silica and promoted with various metals, including Ag, Cu, and Ni. The ethanol conversion over these catalysts ranged from 2% to 90%, and the best performance was obtained with $Ag/ZrO_2-SiO_2$ catalysts with selectivity more than 74% toward butadiene. This group agreed with the mechanism of Quattlebaum and other groups, and they proposed that the aldol condensation step is rate controlling because acetaldehyde was the most abundant intermediate observed during their reactions. In agreement with the group of Kvisle, this group also suggests that the catalyst structure is critical for achieving the highest activity and selectivity toward butadiene. Among the metal promoters studied by this group, metallic Ni showed the best stability, which is related to the avoidance of coke formation in the presence of Ni.

Gruver et al. (1995) have hypothesized a new pathway for conversion of ethanol into butadiene over aluminated sepiolite catalysts at 280°C. In contrast to previous studies, this mechanism involves a Prins reaction between ethylene and acetaldehyde followed by dehydration to generate butadiene. They proposed this mechanism based on trends in the ethylene and butadiene selectivity, which increases proportional to the overall fractional conversion. This group also reported that ethanol dehydrogenation and ethanol dehydration occur at Lewis acid sites, which are required for the Prins mechanism.

Niiyama et al. (1972) have studied ethanol conversion into butadiene using various silica–magnesia catalysts. They tried to explain the reaction mechanism by evaluating different ratios of catalyst components and observed that silica–magnesia with 85% MgO showed the best activity toward butadiene. They also co-fed different reactants (i.e., ethanol, acetaldehyde, crotonaldehyde). This group

concluded that adding either acetaldehyde or crotonaldehyde to an ethanol feed increased the activity toward butadiene, which suggests that both aldehydes are abundant intermediates in the reaction. They also noticed that co-feeding acetaldehyde with ethanol significantly improved the rate of reaction, suggesting that acetaldehyde formation is the rate-determining step. Thus, according to this group, controlling and balancing basic and acidic sites is the most efficient way to maintain catalysts activity and selectivity. Notably, these groups each suggest different reaction networks, indicating that the reaction mechanism is not yet resolved. Further work is needed in this area to elucidate how butadiene is formed from ethanol.

## 3.2 BUTANOL, HIGHER ALCOHOLS, AND AROMATICS

In closely related chemistry, *n*-butanol can be produced by the dimerization of ethanol. Butanol is an important commodity chemical that is normally used as solvent or an additive to gasoline and could be another source for the production of ethers and esters. Butanol is also a "higher alcohol," which is immiscible in water, is noncorrosive, and has a higher energy density than ethanol. Thus, butanol is considered a good potential biofuel.

Currently, butanol is commercially produced from fossil resources by propylene hydroformylation to generate butyraldehyde followed hydrogenation to butanol (Ojima et al., 2004). The use of renewable feedstocks is possible for butanol production, though, either by direct fermentation to yield butanol (e.g., the acetone-butanol-ethanol processes) or ethanol coupling using the Guerbet reaction. Numerous recent studies have focused on the Guerbet reaction, and several types of catalysts with different properties have been developed that lead to butanol production. The reaction network is postulated to be similar to that for the Lebedev reaction (see Fig. 1.1): the alcohol is dehydrogenated to form the corresponding aldehyde, which subsequently undergoes aldol condensation. The resulting unsaturated aldehyde is then reduced to the required alcohol via oxide-mediated H-transfer reactions. Achieving high selectivity to butanol can be a challenge using this pathway (Furukawa et al., 1959).

Riittonen et al. (2012) have probed a wide selection of metals supported on alumina (e.g., Ni, Pd, Au, Rh, Ru, and Ag) for the direct conversion of ethanol into butanol at 250°C. In this work, Ni metal supported on alumina was reported to show the best performance compared with the other metals in terms of selectivity, achieving more than 80% selectivity to butanol at 25% ethanol conversion. In contrast, Dowson et al. (2013) reported a collection of ruthenium-based catalysts of which the best achieved 94% selectivity to butanol at ethanol conversions over 20%. These catalysts are notable because of their high selectivity compared with other systems. These authors also suggest that the base-catalyzed aldol condensation of acetaldehyde is most significant for achieving high selectivity because improving the rate of aldol condensation led to increased butanol selectivity.

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# Exploring the Variety of Random Documents with Different Content

me, it makes us seem more like real sisters instead of just a girl whom Jean's family is befriending."

Gerry nodded, mute for once because Olive had put the case too plainly for her either to add to it or to contradict.

"Dear Jean, it is awfully good of her and awfully foolish and just what I should have expected," she went on. "Please understand that I am very sorry both for Jean's and Frieda's sakes that I ever came with them as a student to Primrose Hall and I would have gone away before now only I could not worry Jacqueline Ralston, who is so ill, or our chaperon, Ruth Drew, who must give all her time and thought to Jack. But you see none of us realized that the girls at Primrose Hall would care so much because my birth and past were so different from theirs. In the West these things do not count to so great an extent."

To her own surprise Gerry Ferrows' eyes, which were seldom given to this proceeding, suddenly filled with tears. Like Ishmael of old, Olive seemed to her to be cast out into the desert for a crime in which she had no part.

But if this Indian girl had always been shy and sensitive in her attitude before the hurt of her schoolmates' coldness toward her in times past, at this moment her manner greatly changed. Perhaps because Olive was so quiet and gentle it had looked as though she had no pride, but this is not true, for her pride was of a deeper kind than expresses itself in noise and protest: it was of that unconscious kind associated with high birth and breeding, the pride that suffers wrong and hurt with dignity and in silence.

Now she drew herself up, facing her companion quietly, her dark eyes quite steady, her lips fixed in a firm line and two bright spots of color glowing in her dark cheeks. "I cannot tell you how much I thank you for telling me this about Jean," she said "and please believe I did not know of it. Of course you wish me to make Jean see the foolishness and the utter uselessness of her sacrifice of herself for me and I surely will. I suppose you must have wondered why I did not do this before."

And still Gerry continued to find conversation increasingly difficult, though fortunately Olive was saying for her the very things she had intended to say. Shyly Gerry slipped her arm in school-girl fashion across Olive's shoulder, but the other girl drew herself away, not angrily in the least, but as if she wished neither sympathy nor an apology.

"Do let us go on back to the house at once," she suggested, "for I must not waste any time before I see Jean, as the election is to take place so soon. If her connection with me should make her lose it I simply don't know what I should do!"

And forgetting all about the presence of Gerry, Olive started for home, walking with that peculiar grace and swiftness which was so marked a characteristic of her training.

Almost panting, Gerry, who was herself exceedingly athletic, tried to keep up. "You must not be foolish, Olive," she begged, "and you are a brick! Whatever happens it can't be your fault if we girls at Primrose Hall are narrow and hateful and blind." For somehow at this late hour in their acquaintance Gerry Ferrows had begun to realize that whatever unfortunate past Olive Ralston may have had, somehow she had managed to breathe a higher atmosphere than most other girls. In their first intimate talk together Olive had shown no anger against her classmates for their cruelty, no envy of Jean's popularity or desire to claim her allegiance as a defense against their unkindness. No, she had only been too anxious to sacrifice herself, to make the way straight for Jean. And at this moment quite humbly Gerry would have liked to have begged Olive to allow her to be her friend, only at this time she did not dare. And as they walked on together in silence some lines that she had learned that morning in their Shakespeare class in their reading of "The Winter's Tale," came suddenly to her mind.

“Nothing she does or seems, but smacks of something greater
than herself,
Too noble for this place.”

# CHAPTER XIV
# "TO THINE OWN SELF BE TRUE"

Fortunately the two girls had not to spend a minute in looking for Jean, for no sooner had they entered the front hall of the school than she was seen talking with a group of friends.

"Hello," she cried, pleased to find that Gerry and Olive had been out together for a walk and grateful for what she thought Gerry's friendliness to Olive.

Olive went straight up to her, too much in earnest to be abashed by the presence of others. "Come on up to our sitting room, Jean," she begged, "for Gerry and I have something to talk to you about that must be decided at once."

It was a pity that Olive must be in such a hurry, Gerry thought a little impatiently, and also a pity that she had used her name in speaking to Jean and plainly wished her to be present at their coming interview, for there was, of course, a possibility that Jean might be a good deal vexed at her interference. But as Jean left her other friends immediately, slipping one arm through Olive's and another through Gerry's and propelling them as rapidly as she could up the broad stairs, what was there for Gerry to do but to surrender and let things take their course?

"Whatever weighty problem there is on your mind, Olive Ralston, that you wish me to help you solve," Jean exclaimed gaily, as they reached their own door, "kindly remember that three heads are better than one, even if one is a dunce's head, else I should never have allowed Geraldine Ferrows to be present at our council." And giving each of the girls an added shove, the three of them plunged headlong into the sitting room.

Frieda was not to be seen, but to their surprise there before their open fire Jessica Hunt sat peacefully, holding a large open box of flowers on her lap, with her cheeks a good deal flushed, possibly from the heat of the fire.

"I beg your pardon, children, for having taken possession of your apartment in this way," she explained, "but I happen to have a present for you sent through my care and it seemed to me that the surest way to find you was to wait at your own hearthstone until you chose to appear." While Jessica was speaking she was holding out the box of flowers toward Jean and Olive. "Mr. Drummond has sent you these with a note to me asking me to see that you get them."

With cries of delight the two ranch girls, pouncing on the great box, which was brimful of violets, buried their noses in its fragrances.

"They are just too lovely and too Rainbow ranchy for anything," Jean exclaimed, thrusting a bunch into Gerry's hand. "Won't Frieda be homesick for her violet beds when she sees them, even if she is so enraptured with boarding school that she hardly talks of home any more?"

While Jean was speaking Olive was busily lifting the flowers from the box. Just toward the last she discovered a separate bouquet, wrapped in white paper and bearing a card with a name inscribed upon it.

"This is for you, Miss Hunt; it has your name upon it," Olive announced, trying to look entirely unconscious, although she and Jean both guessed at once that the gift of the large box of flowers to them had been made largely in order to include the smaller offering inside it.

Jessica, assuming a far-away expression of complete indifference, took the flowers; they were lilies of the valley encircled with violets and it was difficult for any girl to conceal her delight in them.

Watching her with her head slightly to one side and a dangerously demure look on her face, Jean said suddenly, "I wonder, Miss Hunt, how long you have known our Mr. Drummond? You see, we are awfully fond of him and he has been very good to all of us,

especially to Jack. Sometimes I have wondered if he could think you and Jack look a little bit alike? Olive and I think you do. But we don't know anything about Mr. Drummond except that he is terribly rich and terribly good looking and very kind. Can't you tell us something more?"

Jessica shook her head gravely. "I am afraid that is all I can tell you about Peter, I mean Mr. Drummond, that is of any importance. Just that he is rich and good looking and kind. He is so rich that he has never done anything or been anything else, and I have known him a great many years, since I was a small girl and he was a big boy and we used to live near one another in Washington Square, before my father died and we lost some of our money."

"Well," Jean returned reflectively, "it seems to me that it is a good deal to be just rich and good looking and kind, for there are lots of people who are not one of those three things."

And though Jessica was not feeling especially happy at the moment, Jean's words made her smile. "That is true, dear," she returned, "but I am afraid that I want a man to be more and to mean more in this world than just that." She was about to leave the room when Olive put her hand on her arm. "Don't go, Jessica, Miss Hunt I mean," she apologized, "but I so often think of you as a girl like the rest of us. I want to talk to Jean about something and I wish you to stay to help me make her behave sensibly."

Still unsuspicious of what Olive had in mind, but realizing now that it was important, else she would not have called in so many persons to her assistance, Jean put down her flowers and coming up to her friend placed one hand on each of her shoulders, looking closely with her own autumn-toned brown eyes into her friend's darker ones.

"Out with it, Olive Ralston. What on earth is it that you wish me to do that requires so much persuasion?"

And Olive, equally in earnest, likewise put her hands on Jean's shoulders, so that the two girls made an unconscious picture illustrating the old proverb: "United we stand, divided we fall."

"I want you, Jean, please not to be a goose," Olive pleaded.

Gay laughter rang out in response. "I knew, Olive, from the first that you were going to ask me something I could not grant," Jean returned plaintively. "Has any one in this world ever heard of a goose who chose to be one?"

Her listeners could not help smiling, but Olive's mood was too intense for interruption. Without allowing Jean another opportunity for a moment's speech she began her request, imploring her to join the Theta Society at once and not to put it off a day longer than necessary. "For how, dear, can you do me the least good by not belonging when the girls want you so much and when if you don't you may lose your chance at the Junior election," she ended.

"And who, Olive, has been telling you that I am not already a member of the Theta Society and that my chance for the presidency will be influenced if I am not?" Jean inquired angrily, although she did not glance toward any one for her answer save Olive.

But Gerry Ferrows was not in the least a coward, neither did she feel in any sense a traitor either to Jean or to Olive, so now she moved quietly forward.

"I told Olive, Jean," she answered, "and you may be angry with me, but I have no intention of playing a sneak. For the life of me I cannot see how it will hurt Olive for you to join the Thetas without her and it will hurt you very much in your election if you don't. Olive is not going to be invited to become a member if you stay out and you may lose the class presidency if you are so obstinate."

Olive turned to Jessica Hunt. "Won't you please tell Jean that Gerry is perfectly right and that there is no other way of looking at this matter?" she entreated. "She will just break my heart if she does not, and I can't see a bit of sense in her position."

"I can," Jessica answered briefly, "but I would rather not say anything at all until I have heard just how Jean feels about this whole business."

A grateful look was flashed at her, but Jean moved first toward Gerry.

"I am awfully sorry I was cross, Gerry," she murmured, "because of course I know you are being good as gold to me and only acting

for what you believe to be my good, but I don't think either you or Olive in the least understand my position. I am not staying out of the Theta Society for Olive's sake; I am staying out for my own."

"But that can't be possible," both the other girls urged.

"Gerry Ferrows," Jean said, "I want you to do me a favor. I want you to think quietly of what your opinion of another girl would be (leaving me out of the case entirely) if that girl should win out in a big matter like a class election by turning her back on her best friend and more than her friend, her almost sister. And you, Olive, suppose you had no part in this business at all, or suppose you and I had changed places, what would you think of a girl who would say to another group of girls, 'Yes, thank you, I am very grateful indeed to you for permitting me to enjoy your superior society, even if you do think the people whom I love and who belong to my family are not worthy of association with you?' I, of course, am humbly delighted to be a renegade and a traitor if you will just let me play with you." And Jean's brown eyes were flashing and her face was pale, yet she laughed a little at her own fierceness.

"Oh, I won't pretend that I didn't think at first of doing just this thing that you girls are begging me to do," she went on, "and I argued it all out in my own mind that I wouldn't hurt Olive by joining the Theta's, but I never could persuade myself that such an action would not hurt me. See here, dear," and Jean's usually merry lips were trembling as she spoke again directly to Olive. "How could it injure you for me to forget our friendship and happy years together at the ranch, for wouldn't you still be true and loyal and devoted to me? But poor little me, and what would I be? Wouldn't I have to live with myself day time and night time knowing exactly what kind of a wretch I was? No, sir-ee," and here Jean struck a highly dramatic attitude, pretending to slip her fingers inside an imaginary coat. "In the words of that famous gentleman, whether Henry Clay, or Patrick Henry, or Daniel Webster, I can't remember, 'I would rather be right than President!'"

"Bravo, Jean," called Jessica's voice from the doorway, "I take off my hat to you! Gerry, Olive, please don't argue this question any

further with Jean, for she has just said something that we all know to be a fact: 'To thine own self be true. Thou canst not then be false to any man.'"

Gerry cleared her throat, pulling at her short hair rather like an embarrassed boy than a clever girl of seventeen. "All right, Jean," she conceded; "maybe you are right, and of course you are if you feel as you say you do, so I shall not try to make you change your opinion."

But Olive, equally miserable and unconvinced, standing alone in the center of the room, said to Jean, "You are dreadfully good, but I don't care what you say, I simply can't allow you to sacrifice yourself in the way you are doing for me. I must find out how to prevent it and I warn you now that I shall write to Jack and have her ask you to change your mind."

Jean only laughed. "It would be so like old Jack to ask a fellow to be a poor sport," she teased, "but for goodness sake don't let us talk about this tedious subject any longer and do let us put the kettle on and all take tea, for I have talked so much I am nearly dying of thirst."

Around a small table the four girls placed themselves, the ranch girls getting out their tins of cakes and chocolates kept for just such occasions, and nothing more of a serious character was said until they were all comfortably sipping their tea. And then Jean turned to Olive.

"Look here, Olive, I want to ask Gerry a question, if it won't hurt your feelings too much, and while Miss Hunt is here with us it seems to me the best time to ask it. Gerry, of course we have known for some time that there has been some gossip about Olive going the rounds of the school, but we have never known who started it nor just what the story is. Would you mind telling us?"

Instead of answering Gerry hesitated, her homely, kindly face showing nervousness and discomfort.

"Is the story just that Olive does not know who her parents are and that we ranch girls found her several years ago with an Indian

woman and that she may be of part Indian blood?" Jean continued inexorably.

Gerry nodded her head. "Yes, and the story came originally through the Harmons, I believe, though they meant no harm."

"Is that all the tale or has anything else been added?" her questioner continued. And Gerry answered with her eyes on her saucer, "Yes, that is all."

"Then please tell every girl at Primrose Hall that what they have heard is perfectly true," Jean blazed, although she was trying to speak calmly. "I can see now that we have made a mistake; it would have been better if we had been perfectly candid about Olive's past from the first. There never has been a minute when we would have minded telling it, if any one of the girls had come and asked us, but lately I have thought that some extra story must have been hatched up about poor Olive and joined to the true one, for I simply couldn't believe that any human beings could be so horrid and so stupid as the Primrose Hall girls have been to Olive, unless they had been told something perfectly dreadful about her. Well, I don't think I care a snap about being class president of such a set of girls," Jean added impolitely, forgetting one of her guests. "Olive Ralston, I don't believe you are any more an Indian than I am, but I want to say just this one more thing and then I positively promise to stop talking: For my part I would rather have good red Indian blood in my veins than the kind of thin white blood that must run in the veins of such a horrid set of snobs. Gerry, dear, I do beg your pardon and of course I don't mean you, but if I hadn't been allowed to speak this out loud, I should certainly have exploded."

Gerry's head dropped. "Well, perhaps I have belonged to the snobs, too, Jean," she answered truthfully, "but if Olive will forgive me and make up, perhaps some day we may be friends."

Slowly the sitting-room door now opened and a languid figure, clothed in a marvelous dressing gown of pale blue silk and lace, with yellow hair piled high on its head, entered the room. "What on earth is Jean preaching about?" the voice of no other person than the youngest Miss Ralston inquired. "I have just been across the hall

with Mollie and Lucy Johnson and I declare she has been talking steadily for an hour."

Jessica Hunt made some laughing explanation, but Olive and Jean could only stare in amazement at Frieda. Where on earth had she gotten so marvelous a kimono? It really looked like a stage affair. But at this instant, beholding the violets, Frieda, forgetting her grown-up manner for a moment, jumped at them. "Aren't they too beau-ti-ful?" she said like the small girl who once had taken care of her own violet beds at The Rainbow Lodge.

# CHAPTER XV
# THE DANGER OF WEALTH

The truth of the matter was that Frieda Ralston would have been somewhat happier and certainly a great deal better off in many respects could she now have turned back the pages of her existence for a few months and been again that same little yellow-haired girl who was the beloved of every man, woman and child within the thousand acres of the Rainbow Ranch, for Frieda had lately been getting into a kind of mischief that is of a serious nature, whether practiced by a young girl or by very much older persons. She had been spending far too much money.

After the trip to New York and the purchase of the blue silk gown and velvet coat a number of weeks before, the desire for beautiful clothes awoke in Frieda. Remember that she was only a Western ranch girl and had never dreamed of such splendors as the New York shops afforded, neither did she have any very clear idea of the real value of money. Because gold had been discovered on their ranch and because Jack was sending her fifty dollars as pin money each month, Frieda considered that their wealth must be fabulous and so she had contracted the very dangerous habit of buying whatever she wished without considering the cost, and the way she managed to do this was by making bills!

Earlier in the season, when the girls had found it difficult to go into town for every little purchase it became necessary for them to make, Ruth had opened a charge account for the three ranch girls at one of the best of the New York shops, but the bills were expected to be sent to the girls and to be paid out of their allowances. Jean and Olive had made only a few necessary purchases, but though no

one else knew of it, Frieda had lately been buying with utter recklessness.

Indeed, the gorgeous kimono which had just electrified the other two ranch girls was only one of a number of articles that had arrived that very afternoon and been delivered in the care of Mollie Johnson. Hanging up in Mollie's closet at the same instant was an equally charming garment, almost of the same kind as Frieda's, save that it was pink and but lately presented by Frieda to her best friend.

So it would appear that even though Frieda might be keeping the letter of the law in not speaking of their wealth at Primrose Hall, she was certainly not obeying it in spirit, and indeed she had broken her promise altogether on the afternoon when she and Mollie had been alone together, while Olive and Jean were drinking tea at "The Towers."

Not that she had meant to do this when Mollie came in; far from it. The story had just leaked out quite innocently at first. For Frieda naturally began the conversation with her friend by telling her that Jean and Olive had gone to tea with the Harmons, and then that they had learned to know the Harmons because they had rented their ranch to them the summer before. From the ranch the speaker traveled very naturally to the Yellowstone and the story of Jack, told many times before, and coming back again to the ranch ended with Mr. Harmon's effort to buy the Rainbow Mine.

When this word "mine" popped out, Frieda had stopped suddenly, but it was soul satisfying to observe how her friend Mollie's eyes had grown wider and bigger with admiration and surprise at her words. "Why, Frieda Ralston," Mollie had reproached at once, "you don't mean to tell me that you are an heiress as well as everything else that is interesting! Why, you have let me think that you were poor before, though I have wondered sometimes about the lovely things you have been buying. Do please tell me whether your mine is copper or silver or pure gold?"

To Frieda's credit it must be stated that when Mollie thus began her very natural investigation of her story, she felt at once both sorry and frightened. "It is a secret, Mollie," she began; "that is, I don't

see any sense in its being, but I have promised Jack and Jean and Ruth Drew not to talk about our money at Primrose Hall, since we would rather have our friends just know us as ranch girls, but we really have a gold mine. Do you see why I shouldn't talk about it?"

Earnestly Mollie shook her head.

"Well, I suppose I shouldn't, so long as I have promised," Frieda conceded; "but now I have told you of it without meaning to, I am glad, for I do just want to talk about it with somebody and you are my dearest friend and I wish you to know everything about me."

Frieda might have said that she wished Mollie to know all the nice things about her, for it really is not our faults that we long to pour into the ears of our friends.

The invalid, who had been stretched on the couch with a bad cold for the past hour or so, now curled her feet up under her and rested her chin on her hands. "Want me to tell you every single thing about our mine?" she demanded. "It is quite like a fairy story."

And of course there is nobody in the world (and certainly not Mollie Johnson) who does not like to hear of the finding of a mine.

"Cross your heart and body that you'll never betray me; say you wish you may die if you do," Frieda abjured. And promising everything and making all the mystic signs necessary to eternal secrecy, Mollie then had listened to the unfolding of the fairy tale.

Frieda had not really intended to make her story a fairy tale, but she had no more idea of how much money the Rainbow Mine produced than a baby, and of course with the telling of her tale the size of the nuggets that Jim was getting out of the mine each week naturally grew.

"You see," Frieda explained, warming with her subject, "we simply don't know how rich we are. Jim, our overseer at the ranch, who now looks after our mine, says you never can tell at first how much a mine may yield. Perhaps we may be millionaires some day."

The word millionaire was an entirely new one in Frieda's vocabulary, which she had learned since coming to Primrose Hall, but certainly it had a magnificent sound and made Mollie blink.

"It sounds just too wonderful," the little Southern girl sighed, "and I do declare, Frieda, that if I didn't love you more than most anybody I should feel envious. We aren't rich a bit; my father is just a lawyer in Richmond and while we have a pretty house and all that, why we have some other brothers and sisters, and father says all he can afford to do is to let Lucy and me have two years apiece at Primrose Hall. He can't give us money for the wonderful clothes you buy. Won't I be proud if you can make me a visit in the Christmas holidays to show you and your lovely things to my friends!" And Mollie began twisting into curls the ends of her Frieda's yellow braids and looking up at her with an even increased admiration.

Such a rush of recklessness and affection then seized hold on the youngest Miss Ralston, that without even discussing the question with Mollie, she immediately arose from her couch and rushing to her desk indited a letter to a New York firm asking that the two kimonos be sent her at once with slippers and stockings to match. For her beloved Mollie was just too sweet and sympathetic for anything and quite unlike adopted sisters and relations, who scolded and put on airs when one's affairs went a bit wrong. Frieda would have liked at the instant of writing her letter to have poured all her wealth at her friend's feet, but all that she could do more was to invite her to come into town the next week to be her guest at the matinee and lunch and to help her make a few more purchases.

For Frieda's December bill had not yet arrived and her check had, and so for the time being, like many another person, she felt fairly well off, although her allowance for the past two months had melted away like wax without her being able to pay back a single cent of the money to either Jean or Olive, which they had advanced to help with her first extravagance, the blue silk dress and velvet coat.

One of the subjects that a great many people discuss, with a good deal more money at their disposal than Frieda had at present, is the way that five-dollar bills have of disappearing in New York City. So by the time Frieda had paid for three tickets to the matinee, as the girls were of course compelled to bring a chaperon into town with them, and three lunches at a fashionable restaurant, there was

so little of her money left out of her original amount that again she was obliged to do some charging on her account, in order to get the few more things that she and Mollie decided might be needed in case she paid the visit in Richmond toward the close of December.

On the way back to Primrose Hall, however, seated on the train and feeling a bit weary, Frieda wished that she had not spent this extra money. Now she wouldn't be able to pay her debts until January, and what with Christmas coming, there would be so many presents for others that she would wish to buy! So once Frieda sighed, but when Mollie, giving her a hug, demanded to know what worried her, she would not say. For how confess that money matters were worrying her but a few days after the time when she had announced herself as an heiress? Of course Jack and Ruth would see that she was supplied with extra money at Christmas time, if they should consent to let her make the trip south, and out of this amount she would certainly save enough to pay her bills, without having to confess her extravagances. For Frieda knew that Jack and Ruth would both be angry and ashamed of her for breaking her promise and for buying things which she did not really need.

# CHAPTER XVI
# ELECTION DAY

The day for the election of the president of the Junior Class had arrived at last. Lessons were over at noon and from three o'clock until six in the afternoon Jessica Hunt and Miss Sterne would remain in the library at Primrose Hall watching over the ballot box. Immediately after six the box would be opened, the ballots counted and the choice of the Juniors announced.

For December had come with her white frosts and cold, brilliant days and the fields about Primrose Hall were sere and brown. Now and then in the past few weeks a light snow had fallen and the shore waters of the Hudson River would then be trimmed with a fine fringe of ice. Once the election was over the Primrose Hall students would be making plans for the Christmas holidays, but until then nothing else, not even home and family, appeared of so great importance.

Do not think because Gerry's appeal to Olive to save Jean had gone astray that she had given up the fight for her friend's cause. Indeed, like many another brave campaigner, she had only worked the harder, rallying Jean's friends closer around her, exhorting her enemies and trying to persuade the girls on the fence that there was no real point in their antagonism toward Olive. And in all the efforts Gerry had made she had had an able lieutenant in Margaret Belknap, Jean's other devoted friend.

For herself Jean could do little electioneering, realizing that unless her classmates desired her to represent them by reason of the character she had already established among them, nothing she could do or say at this late day should influence them. And Jean had

also never wavered from the attitude she had taken in regard to Olive on the afternoon of their final discussion of the subject. She had not needed that her resolution be strengthened, but if she had, letters from Ruth Drew and Jack Ralston would certainly have accomplished it. For Olive, true to her threat, had written them the entire situation, begging that Jean be persuaded from the error of her ways. Instead of the reply she hoped for, Ruth and Jack had both emphatically declared Jean's position the only possible one.

All the morning in the hours just before the election Jean had been conscious that Olive's eyes were fixed on her whenever their presence in one of the class rooms made it possible. Her expression was so wistful and apologetic that Jean began to care more for her own success on Olive's account than her own. So as soon as luncheon was over and three o'clock had come around, slipping her arm through her adopted sister's, she drew her along the hall toward the library door.

"Come on, Olive, child, and cast your vote for me and then let us go upstairs and stay hidden away until the election is over. Then Gerry and Margaret will let us know the result. If I were a really high-minded person I suppose I should now vote for my rival, Miss Graham, but as I can't bring myself up to that point, I'll just slip in a piece of paper for old Gerry."

Ten minutes after this conversation Jean and Olive were in their own sitting room for the entire afternoon, having placed a sign outside announcing that no one could be admitted. Of course both ranch girls were excited and nervous, but of the two Olive was plainly the more affected, for while Jean talked and laughed in a perfectly natural fashion, she was pale and silent and oftentimes on the verge of tears.

The day was cold and lovely and outside the sun shone on the bare upturned branches of the trees and on the broad bosom of the earth.

"Silly child," Jean began, arranging her paper and ink on the writing table before one of their windows, "why should you behave as though the question of my election was the only important thing

in the world. On a day like this I only feel desperately homesick for Jack and the old ranch. What wouldn't I give if we were all there to-day and just starting out on a long, hard ride? Sometimes I am so desperate about never seeing Jack that I don't know what to do. I think I will write to Jim and to Ralph Merrit this afternoon, for it will help to make the time pass faster than anything else. I am afraid I have treated Ralph rather badly, as I promised to write him often and have only written twice. Then I want to ask Jim if he is really coming east to see how Jack is getting on. I wonder if he will hate to see Ruth again or like it? One never can tell about a person in love."

Perhaps Jean's thought of her old friends and affairs at the Rainbow Ranch may have had a cheering influence upon her, for no sooner had she put her pen to the paper than apparently all worry and suspense left her and she scratched away rapidly and clearly for several hours.

But poor Olive found no such distraction or solace; indeed, she kept up such a restless and unnecessary moving about the room that at any other time Jean most certainly would Lave scolded. First she tried studying her Shakespeare, since she was making a special effort to succeed in the Shakespeare class, and before coming east to school had read only a few plays with Ruth and the ranch girls in the big living room at the Lodge. But not the most thrilling historic drama nor the most delightful comedy by William Shakespeare could to-day take her mind from the one idea that engrossed it. After half an hour of merely pretending to read, she flung her book down on the floor, saying petulantly: "Tiresome stuff! I wonder what ever made me think for an instant I could stand any chance of getting the Shakespeare prize?"

Jean smiled. "Oh, I suppose, Olive, because Ruth and all of us thought you had a lot of talent for reciting and acting and you dearly love to read and study at most times. But why don't you go out for a walk, you can find Frieda somewhere around downstairs and make her go with you. I don't want to."

"And I don't want to either and won't," Olive answered with a good deal more temper than usual with her, and flying into her own

room, she banged the door behind her. Rummaging about for some occupation, she came across a piece of sewing which she had once started at the Lodge, some white silk cut in the shape of a round cap to be covered over with small white pearl beads.

Slipping back once more into the sitting room, Olive found a low stool by the fire and there tried to see whether sewing would have a more soothing influence upon her than reading for the two more hours that had somehow to be disposed of. Yes, sewing on this occasion was more distracting than reading, for very soon Olive's fingers worked automatically while her brain began to concern itself with interesting and puzzling ideas. The many hours which she had spent alone at Primrose Hall had not been wholly unprofitable—lonely hours need never be unless we choose to make them so—but Olive perhaps had more to think of and to ponder over than most girls of her age who have not led such eventful lives.

After her afternoon call at "The Towers" and her conversation later with Miss Winthrop, Olive had been reading all the books in the school library that she could find, which might help her explain the curious experience—confided to no one—through which she had passed that afternoon. But it was not just this one experience that had puzzled and worried Olive, for many strange fancies, impressions, memories, she knew not what to call them, had been drifting into her mind since her first sight of that white house on the hill on the morning after her arrival at Tarry dale. The ideas had no special connection with anything that was definite, but Olive was lately beginning to believe that she could recall dim ideas and events having no connection with the years she had spent in the Indian tent with old Laska. But why had these far-off memories not assailed her in the two years at the Rainbow Ranch? Perhaps then the recollection of Laska, of her son Josef, who had treated her with such an odd mixture of respect and cruelty, of the Indian people about her whom she had so disliked, had been too close, too omnipresent in her mind. Had she needed to come far away from the West and its associations to feel that she had come home? No, it

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